13

INFRARED STUDY OF EFFECT OF ENVIRONMENTS ON HYDROGEN BONDING IN CATECHOL, RESORCINOL AND QUINOL

D. K. MUKHERJEE AND S. B. BANERJEE

OPTICS DEPARTMENT,

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

CALCUTTA-32.

(*Received June*, 13, 1966)

ABSTRACT. The infrared absorption spectra of catechol, resorcinol and quinol have been measured in the solid state and in solution in different solvents. The results confirm the existence of *cis* and *trans* molecules of catechol postulated by previous workers. It has been concluded that in the solid state the catechol molecules are intermolecularly linked with each other through hydrogen-bonding while in the case of solutions intermolecular hydrogen bonds of different strengths are formed between catechol and solvent molecules. The intramolecular bond is, however, found to persist with sufficient strength in solutions. The observed solvent effects on the OH vibrational frequencies of resorcinol and quinol have also been explained in terms of formation of intermolecular hydrogen bonds of varying strengths between the solvent and the solute molecules. In the case of resorcinol in the solid state, existence of strongly associated polymeric groups of molecules formed through intermolecular hydrogen bond of bent type as indicated by the structure of the crystal reported by previous workers has been confirmed.

INTRODUCTION

The infrared absorption spectra of catechol and resorcinol were studied in the first harmonic region of OH vibration by Wulf and Liddel (1935), who observed two peaks at 7060 and 6770 cm^{-1} in the case of catechol. In explaining the two peaks Pauling (1936) suggested the existence of *cis* and *trans* molecules of catechol. For resorcinol Wulf and Liddel observed only one peak at 7050 cm^{-1}. Ingraham *et al.* (1952) identified the two absorption bands due to free and intramolecularly bonded OH groups in catechol at 3611 and 3568 cm^{-1} respectively. Bellamy *et al* (1966) observed a new peak due to OH vibration at 3535 cm^{-1} in the infrared absorption spectrum of resorcinol in ether and concluded that resorcinol molecules form complexes with ether molecules. Stanevich (1964) found that crystals of resorcinol and quinol exhibit peaks at 3270 cm^{-1} and 3275 cm^{-1} respectively. However, he apparently did not discuss the result for resorcinol by considering the crystal structure of this compound reported by Robertson (1936). It also appears that no systematic comparative study of the influence of different solvents on the OH vibrational frequencies of the three hydroxy phenols, viz., catechol, resorcinol and quinol has been made by previous workers. The importance of

specific local interaction in accounting for changes in the frequencies and intensities of bands due to groups like OH, C = O, etc., has recently been emphasised by different authors (e.g. Bellamy *et al*, 1958; Caldow and Thompson, 1960). Such a study of solvent effect on OH vibration of the hydroxyphenols would be helpful in ascertaining the nature and strength of intramolecular hydrogen bond in pure substances and would furnish interesting information about specific groups involved in intermolecular bond formation in the case of solutions. The infrared spectra of catechol, resorcinol and quinol have therefore been examined in the pure state and in solutions in different solvents and the results, with probable interpretation, have been presented in this paper.

EXPERIMENTAL

The compounds were obtained from E. Merck and were of AR quality. They were further purified by repeated crystallisation from ether solution and later by sublimation under vacuum. The solvents were carefully purified and dried before use. Thin solid films of catechol and resorcinol were used to record the absorption spectra while the spectrum of quinol in the solid state was measured in nujol mull.

The spectra were recorded with a Perkin Elmer Model 21 spectrophotometer fitted with rocksalt optics. The calibration was checked by recording the atmospheric water vapour band at 3740 cm^{-1}.

RESULTS AND DISCUSSION

The observed vibrational frequencies are given in Tables I, II and III. The absorption spectra of the compounds in pure state and in different solutions are

TABLE I

Catechol : O–H vibrational frequencies in cm^{-1}

	Solution in				
Solid at 70°C (thin film)	C_2Cl_4 (Ingraham et al. 1952)	$CHCl_3$	C_6H_6	$C_6H_5NO_2$	$(C_2H_5)_2O$
	3611	3614	3590		
3545	3568	3565	3560	3560	3565
				3525	
3440					3320

TABLE II

Resorcinol : O–H vibrational frequencies in cm^{-1}

Solid (Stanevich, 1964)	Solid at 25°C (present authors)	Solution in $(C_2H_5)_2O$	Solution in C_6H_6	Solution in $CHCl_3$	Solution in $C_6H_5NO_2$	Ether-resorcinol soln. dissolved in benzene
			3580	3595	3580 3515	3585
		3335				3325
3270	3270					

TABLE III

Quinol : O–H vibrational frequencies in cm^{-1}

Solid (Stanevich, 1964)	Solid in Nujol mull (present authors)	Solution in $(C_2H_5)_2O$	Ether-quinol solution dissolved in benzene
			3595
		3385	3360
3275	3260		

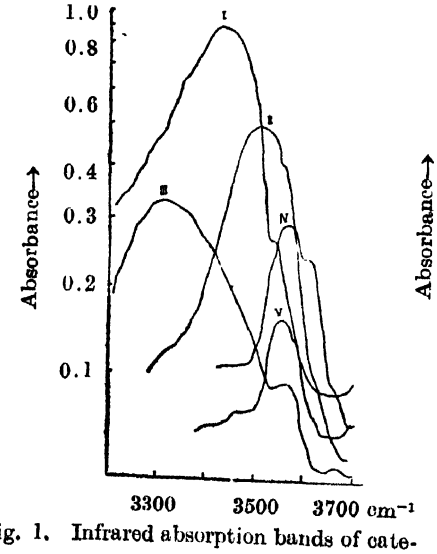

Fig. 1. Infrared absorption bands of catechol.

I. Solid at 70°C (thin film).
II. 0.6 M Solution in nitrobenzene
III. 0.8 M „ „ ether
IV. 0.3 M „ „ chloroform
V. 0.8 M „ „ benzene

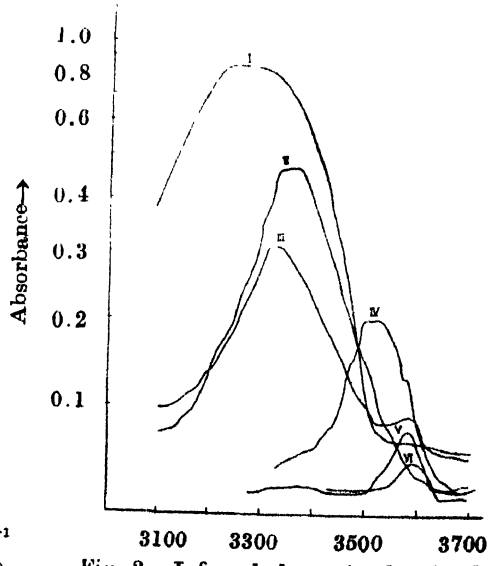

Fig. 2. Infrared absorption bands of resorcinol.

I. Solid at 25°C (thin film)
II. 0.8 M Solution in ether
III. 3% ether-resorcinol complex in benzene
IV. 0.6 M Solution in nitrobenzene
V. 0.8 M „ „ benzene
VI. 0.3 M „ „ chloroform

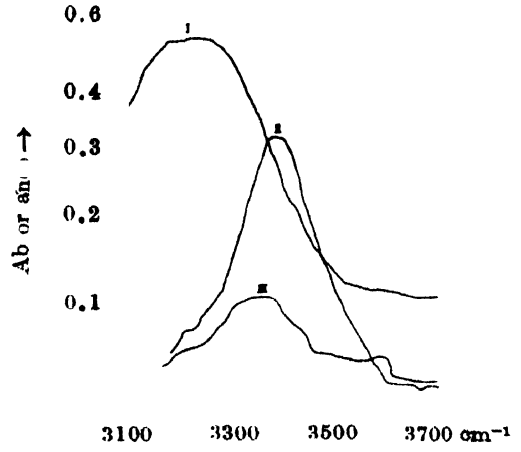

Fig. 3. Infrared absorption bands of quinol.

I. Solid in nujol mull

II. 0.6 M Solution in ether

III. 1% ether-quinol complex in benzene.

reproduced in Figs. 1, 2 and 3. The results for the three compounds are discussed separately in the following paragraphs.

Catechol :

In dilute solutions in chloroform and benzene two peaks due to the stretching frequencies of free and intramolecularly bonded OH group corresponding to the *trans* and *cis* configurations postulated by Pauling (1936) could be identified. In chloroform solution the former is at 3614 cm^{-1} and the latter is at 3565 cm^{-1} while in the benzene solution the free OH stretching band is at about 3590 cm^{-1}, the frequency of the bonded OH being 3560 cm^{-1}. The slight decrease of the stretching frequency of the free OH vibration probably indicates slight basic behaviour of benzene to the hydroxyphenol. In ether solution, the band due to free OH vibration is absent and a new strong peak at 3320 cm^{-1} is observed. Evidently, this new band arises from association of molecules of ether with catechol through hydrogen-bonding between oxygen of ether and an O–H of catechol. In nitrobenzene also, the proton acceptor NO_2 group forms weak hydrogen bond with catechol molecule as is evident from the disappearance of the free OH vibrational band and appearance of a new band at 3525 cm^{-1}. In both ether and nitrobenzene solutions, the band due to intramolecularly bonded OH vibration persists with sufficient strength to indicate that the intramolecular OH ... 0 bond in catechol is strong enough to resist the influence of strong proton-accepting groups in solvents tending to break it up and that the intermolecular hydrogen

bond between the solvent and solute molecules is formed through the free OH group of the catechol molecule (Figs. 4 and 5).

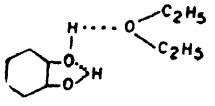

Fig. 4

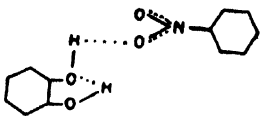

Fig. 5

In the case of crystals of catechol at 25°C only a broad strong band at 3440 cm^{-1} is observed. When the temperature is raised to about 70°C a second weak hump at about 3545 cm^{-1} is observed. This latter band obviously represents the stretching mode of the intramolecularly bonded OH. The new band at 3440 cm^{-1} can then be attributed to the formation of intermolecular OH ... O bond between neighbouring molecules in the solid state (Fig. 6).

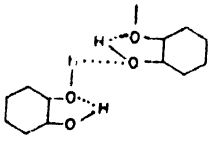

Fig. 6

The above findings apparently corroborate the views of previous authors (e.g. Bellamy and Pace, 1966) that formation of an O–H ... O–H bond makes the hydrogen attached to the acceptor oxygen more acidic and the oxygen of the donor OH group more basic, thus increasing the probability of formation of hydrogen bond at either end.

Resorcinol

In this molecule with two hydroxyl groups in the meta position there is no possibility of formation of intramolecular hydrogen bond and in chloroform solution the absorption band due to the free OH vibration appears at 3595 cm^{-1}, while in benzene solution this band is at 3580 cm^{-1}, which again shows slight displacement towards lower energies. In ether solution only a strong broad band with its centre at about 3335 cm^{-1} is observed. This band could be readily identified with the stretching vibration of the hydroxyl group hydrogen-bonded with oxygen of the ether molecule. This result is in agreement with that of Bellamy *et al.* (1966). When the resorcinol-ether complex is dissolved in benzene, probably some of the intermolecular bonds break up, as is apparent from appearance of a weak band at 3585 cm^{-1} due to free OH group. In nitrobenzene solution the existence of both free OH group and intermolecularly associated OH group weakly

bonded with the nitro group is evident from the appearance of two peaks at 3580 and 3515 cm^{-1} respectively. The absorption band of thin solid film is very broad with its centre at about 3270 cm^{-1}, which shows that the OH groups of neighbouring molecules are intermolecularly linked through OH ... 0 bond. The frequency of the intermolecularly bonded OH group in the solid state is lower than that of the OH group linked with oxygen of the ether molecule in ether solution. This fact and the large width of the OH band could evidently be attributed to the presence of polymeric chain of intermolecularly OH ... O bonded resorcinol molecules in the solid state. It would be interesting to note that from an investigation of crystal structure of resorcinol Robertson (1936) concluded that in the crystal, the molecules of resorcinol are grouped in spiral arrays about the two-fold screw axes and the hydroxyl groups of successive pairs of molecules approach each other to within a remarkable short distance of 2.7A, which indicates presence of hydroxyl bonds, the angles between the bonds being fairly near the tetrahedral value of 109.5°. The results of the present investigation are thus in good qualitative agreement with Robertson's conclusion. The structure of the crystal further shows that the intermolecular OH ... O bond is of bent type. In that case the strong hydrogen bond which is responsible for the large frequency-shift could be attributed to the special cyclic structure of the associated molecules as discussed by Bellamy and Pace (1966).

Quinol

The infrared absorption spectrum of this compound in dilute solution should contain only one band due to free OH vibration, as there is no possibility of intramolecular hydrogen-bonding between OH groups which are in para position in the molecule. In ether solution a strong absorption band at 3385 cm^{-1} is observed. From a comparison with spectra of the other two hydroxyphenols this band could be attributed to the vibrational frequency of the OH group hydrogen-bonded with the oxygen of ether which forms a complex with quinol. When the ether-quinol complex is dissolved in a very dilute solution in benzene this band shifts slightly towards lower frequencies and a very weak band at about 3595 cm^{-1} is just discernible. This last band probably represents the frequency of free OH vibration. In the absorption spectrum due to the crystals dispersed in nujol mull a very broad absorption band with its centre at about 3260 cm^{-1} is observed. A similar maximum at 3275 cm^{-1} was reported by Stanevich (1964) for the quinol crystals. As for resorcinol, such absorption points to the presence of intermolecularly hydrogen-bonded polymeric molecules of quinol in the solid state.

ACKNOWLEDGMENT

The authors' thanks are due to Professor S. C. Sirkar, D.Sc., F.N.I. for helpful discussion and to Professor G. S. Kastha, D.Sc. for kindly offering facilities for

the work. Financial support to one of the authors (S.B.B.) as Pool Officer by the C.S.I.R., India is acknowledged.

REFERENCES

Bellamy, L. J., Hallam, H. E., and Williams, R. L., 1958, *Trans. Faraday Soc.*, *54*, 1120.
Bellamy, L. J. and Pace, R. J., 1966, *Spectrochim Acta*, *22*, 525.
Caldow, G. L. and Thompson, H. W., 1960, *Proc. Roy. Soc.* (*London*), *A 254*, 1.
Ingraham, L. L., Corse, J. and Bailey, G. T., 1952, *J. Am. Chem. Soc.*, *74*, 2297.
Pauling, L., 1936, *J. Am. Chem. Soc.*, *58*, 94.
Robertson, J. M., 1936, *Proc. Roy. Soc.* (*London*), *A157*, 79.
Stanovich, A. E., 1964, *Optik i Spektros.*, *16*(*6*), 998.
Wulf, O. R. and Liddel, U., 1935, *J. Am. Chem. Soc.*, *57*, 1464.